



Li-doped mixtures of alkoxy-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)-imide and organic carbonates as safe liquid electrolytes for lithium batteries

I. Quinzeni, S. Ferrari, E. Quartarone*, C. Tomasi, M. Fagnoni, P. Mustarelli

Dept. of Chemistry and INSTM, University of Pavia, Via Taramelli 16, 27100 Pavia, Italy

HIGHLIGHTS

- Li-doped mixtures of alkoxy-PYR-TFSI and organic carbonates as safe electrolytes.
- Non-flammable mixtures with $\sigma > 7 \text{ mS cm}^{-1}$ at 20 °C and r.t. η lower of 25 cPs.
- Good performances of the best mixture at 1 C for 250 cycles with $\sim 100\%$ efficiency.

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ABSTRACT

The availability of safer electrolytes is an important target in the development of the new lithium batteries. The use of Li-doped mixtures based on ionic liquids and organic carbonates seems to be a very promising approach, because it allows to balance the non-flammability, high conductivity, low viscosity and good electrochemical stability.

Here, we reported on the characterization of electrolytes solutions based on *N*-methoxyethyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)-imide (PYR_{1,201}TFSI), EC/DEC binary system and LiTFSI, as potential safe electrolytes for lithium batteries. The mixtures were studied in terms of flammability tests, thermal features, physical properties, namely conductivity and viscosity, and electrochemical performances. We also carried out a comparison with the pure IL–Li salt system as well as with the standard electrolyte 1.0 M LiPF₆ EC–DEC.

The best solution showed ionic conductivity exceeding 7 mS cm^{-1} at 20 °C, room temperature viscosity lower of about 25 cPs and an overall electrochemical window of 4.5 V. With respect to the pure LiTFSI–IL electrolyte, a very stable interface with Li anode was also observed in at least for 20 storage days. This mixture was tested in a LiFePO₄-based cell, and showed good performances at 1 C, assuring electrochemical stability for about 250 cycles with $\sim 100\%$ efficiency.

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1. Introduction

The development of safer lithium batteries represents one of the most important challenges in the field of energy storage, especially in view of the massive applications of these devices in hybrid electric vehicles (HEVs) and plug-in HEVs [1–4]. The liquid electrolytes, conventionally used in the cells, consist of a lithium salt dissolved in linear or cyclic organic carbonates (OCs) or mixtures of

them [5]. Despite the well-known advantages offered by these solvents, firstly the long-life cycling performances, their use is somehow limited by the high flammability and volatility, which seriously lower the safety levels of the battery. Room temperature ionic liquids (RTILs) could be an interesting alternative to the OCs, due to low volatility, non-flammability, high thermal stability and wide electrochemical windows [6–9]. Among the wide spectrum of investigated systems, pyrrolidinium cations were deeply considered for their improved air stability, hydrophobicity, thermal stability up to at least 300 °C and promising ionic conductivity exceeding 2 mS cm^{-1} at r.t. Further, an overall electrochemical window larger than 5 V was observed.

In spite of these interesting properties, the viscosity of the ionic liquids is higher than that one of OCs and, consequently, the

* Corresponding author. Tel.: +39 (0)382 987894; fax: +39 (0)382 987776.
E-mail address: eliana.quartarone@unipv.it (E. Quartarone).

conductivity is lower, in particular in presence of a Li salt [10–12]. One possibility to overcome this limit is the modification of the cation structure by replacing the typical alkyl- side chain with an alkoxy-based one, containing one or more oxygen units. Basically, the use of ether groups as lateral substituents decreases the IL viscosity. Through this way, in fact, viscosity values lower than 30 mPa s and conductivity higher than 2.5 mS cm^{-1} may be easily reached at 20°C in the alkoxy-derivatised ILs, by modulating the nature of the cation ring, the number of oxygen as well as the chain length [13–16]. Other important properties may be also obtained by introducing alkoxy moieties in ILs. The presence of ethers, for instance, hinders the crystallization below room temperature providing amorphous systems. Further, the polarity and the salt solubility are remarkably improved.

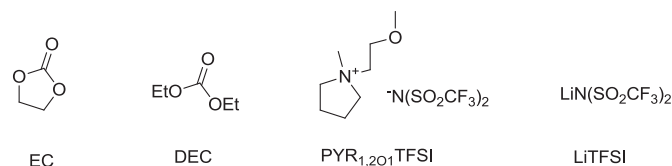
Another interesting approach, recently explored by several researchers, does foresee the addition of proper amounts of organic carbonates to the ionic liquids [17–23]. The use of such mixtures seems to offer several advantages, coming from the combination of the beneficial effects of both the ionic liquids and the co-solvents. First, a decrease of viscosity and a consequent enhancement of conductivity may be planned by using proper volume ratios among the solvents, preserving in the mean time the ILs safety features [17,20]. In addition, the quality of the passivation layers at the anode, particularly in presence of graphite, as well as the overall IL electrochemical properties are improved [18,19]. Even, the thermal stability of the mixtures results to be improved, due to the decrease of the electrolyte crystallization temperatures and, in some case, to the increase of the evaporation/degradation ones, so, extending the operative working range of the battery [17,18]. Finally, the use of such IL–OCs mixtures may overcome some problems showed by the pure ionic liquids about a poor wettability of the separators [21].

In the present paper, we report a physico-chemical and electrochemical investigation of mixtures prepared with an alkoxy-substituted pyrrolidinium, namely *N*-methoxyethyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)-imide (PYR_{1,201}TFSI), and EC:DEC (1:1 v/v) binary systems in a composition range of 100–50 vol%. This ionic liquid was selected due to its low viscosity, ($\eta_{20^\circ\text{C}} = 40 \text{ cP}$) and promising ionic conductivity ($\sigma = 2.9 \text{ mS cm}^{-1}$ at 20°C) [13,15]. Liquid electrolytes were obtained by dissolving LiTFSI, as the Li source, in a molar concentration equal to 0.5 M. The solutions were investigated by means of thermal analysis, viscosity and conductivity measurements, electrochemical stability windows and, finally, flammability tests. The properties of the mixtures were compared to those of both PYR_{1,201}TFSI–LiTFSI (0.5 M) and commercial EC:DEC LiPF₆ (1.0 M) electrolyte. Finally, the resulting best solution was used in combination with Li anode and LiFePO₄ cathode in order to evaluate its cell behaviour.

2. Experimental

2.1. Li-doped mixtures preparation

EC/DEC (1:1 v/v, Ferro Corp.) was used as received, whereas the ionic liquid, *N*-methoxyethyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)-imide (PYR_{1,201}TFSI), was synthesized as already described in detail elsewhere [13]. Three electrolytes, labelled in the following as MIX50, MIX60, MIX70, MIX100, were prepared by mixing proper amounts of IL and EC:DEC in a dry-box (MBraun O₂ < 1 ppm, H₂O < 1 ppm), under argon atmosphere. LiTFSI (Aldrich) was used as Li⁺ sources, and its concentration was kept constant at 0.5 M for each electrolyte. Scheme 1 and Table 1 report the chemical structures of the components and the investigated compositions, respectively.



Scheme 1. Chemical structure of the mixture components.

2.2. Characterization

Differential Scanning Calorimetry (DSC) measurements were performed with a 2910 MDSC (TA Instruments), at a rate of 5°C min^{-1} under nitrogen purge by using either standard or hermetic aluminium pans according to the analysed sample. Thermogravimetric analysis (TGA) measurements were carried out at 5°C min^{-1} under N₂ purge in a 2950 TGA (TA Instruments). The viscosity, η , was measured at 20°C with a cone-plate rotational viscosimeter (Rheotec) in control-shear-stress (CSS) mode. The flammability of the electrolytes solutions was examined by directly observing the formation of a flame on the liquid surface for few seconds, according to the procedure reported in Ref. [17].

The ionic conductivity was measured by means of the impedance spectroscopy technique, using a frequency response analyser (FRA Solartron 1255), connected to an electrochemical interface (Solartron 1287), over the frequency range 1 Hz–1 MHz, by applying a voltage of 100 mV. The impedance scans were carried out in the temperature range between -20°C and 80°C , by using a two-probes liquid cell with platinum electrodes and a cell constant of 0.35 cm^{-1} .

Linear voltammetry was performed by means of an Electrochemical Interface Solartron 1287 with a three-electrodes cell, using lithium as both the counter and the reference electrodes, and nickel as the working one. A Whatman glass microfiber filter was used as the separator. The r.t. electrolyte stability against lithium was investigated by monitoring the time evolution of the impedance response in a symmetric Li/electrolyte/Li cell.

2.3. LiFePO₄ cathode preparation and cell assembly

The performance of the gel polymer electrolytes was evaluated in Li/LiFePO₄ cells. LiFePO₄/C cathode material was prepared by hydrothermal synthesis, as reported in a previous work [24]. The positive electrode was fabricated by spreading a mixture of LiFePO₄ (70 wt%), carbon black (20 wt%) and PVdF (10 wt%) in *N*-methyl-2-pyrrolidone, onto Al foil as current collector and drying overnight at 80°C . The film was cut in disk of 1 cm diameter and the mass loading was about 2.5 mg. The electrochemical tests were performed using a three-electrodes T-cell, with lithium metal as the negative electrode. All the cells were assembled in the dry-box under Argon atmosphere. The galvanostatic cycling tests were carried out with an Arbin battery cycler (model BT-2000), between 2.5 and 4.0 V. The cells were charged and discharged at room temperature in the C rate range between 0.05 and 2 C.

3. Results and discussion

3.1. Flammability and thermal features of the electrolytes

Flammability tests were performed on the investigated IL–EC/DEC mixtures in order to know how the addition of a non-flammable ionic liquid may affect the flammability and volatility of the organic carbonates. As already stated in the experimental part, the mixture flammability was studied by directly observing

Table 1
Physical and electrochemical parameters of the electrolytes: glass transition temperature, T_g ; conductivity, σ , measured at 20 °C; VTF fitting parameters, B , A and T_0 , with the fit goodness, r^2 . The LiTFSI concentration was 0.5 M in each mixture.

Electrolyte	PYR _{1,201} TFSI (Vol%)	EC/DEC 1/1 v/v (Vol%)	T_g (K)	T_0 (K)	B (K)	A (S cm ⁻¹)	r^2	$\sigma_{20^\circ\text{C}}$ (mS cm ⁻¹)
MIX100	100	0	188 ± 2	170	568	0.10	0.998	1.3
MIX70	70	30	181 ± 1	170	414	0.16	0.996	8.0
MIX60	60	40	168 ± 1	118	845	0.90	0.999	7.0
MIX50	50	50	151 ± 1	150	537	0.13	0.994	8.2

the formation of a flame on the liquid surface, as suggested by Zaghib et al. [17]. Fig. 1 reports the photographs of a direct flame on both the MIX60 electrolyte (c, d) and the commercial EC:DEC LiPF₆ 1.0 M solution (a, b). As expected, the commercial electrolyte is highly flammable and easily ignited in few seconds, after the contact with the flame. A remarkably reduced flammability was, in contrast, observed in case of the MIX60 mixture. Further, similar behaviour was showed by the other investigated solutions, namely MIX50 and MIX70, when exposed to the direct flame. The flammability tests were similarly carried out also for the non-doped IL:EC/DEC mixtures (with no Li salt present) in the EC/DEC composition range between 20 and 80%. We observed that the “non-flammable” threshold is obtained when an IL amount higher than 40 vol% is added to the OC mixture, in fair agreement with what reported by Zaghib and co. for mixtures containing organic carbonates and EMI-TFSI as the ionic liquid [17].

The DSC scans performed on both the Li-doped ionic liquid and the mixtures, not reported here, showed three thermal features:

- a glass transition (T_g), detectable at temperatures lower than 200 K, which depends on the amount of the organic carbonates in the mixture;
- an exothermic phenomenon around –25 °C, probably due to cold crystallisation, observed in all the solutions, but in case of Li-doped IL (MIX100). This feature may be likely ascribed to the formation of some complexes between the ionic liquid and the organic carbonates, depending on the mixture composition. The crystallization enthalpies, in fact, decrease with the IL content in the solution, ranging from 7.6 kJ g⁻¹ (for MIX70) to 0.2 kJ g⁻¹ (for MIX50);

- endothermic features above room temperature, peaked around 100 °C, which may be reasonably related to the OCs evaporation. This is, further, confirmed by the thermogravimetry analyses. Fig. 2 reports, as an example, the thermogram of MIX60 in the temperature range between r.t. and 600 °C. The plot of PYR_{1,201}TFSI–LiTFSI 0.5 M (MIX100) system is also shown as a comparison. In the case of MIX60, an almost continuous two-stages weight loss down to about 40% is observed between 30 °C and 200 °C, as somehow expected by considering the intrinsic high volatility of the organic solvents. Comparable weight changes were also discussed by other authors on similar systems [17,19]. Both MIX60 and MIX100 show degradation phenomena starting at about 400 °C.

As already stated before, a glass transition occurs below room temperature in each system. Table 1 reports the T_g values as a function of the IL content in the mixture. A gradual decrease of the temperature may be noted by increasing the amount of the OCs, and this effect is due to the plasticising feature of the organic solvents. In particular, a decrease of the glass transition temperature of about 40 °C with respect to the pure LiTFSI–IL is obtained in case of the electrolyte MIX50.

3.2. Viscosity and ionic conductivity

In order to investigate the role of the OCs binary system on the viscosity and transport properties of PYR_{1,201}TFSI and to select the solvent optimal composition for application as electrolyte, measurements of η and σ were preliminary carried out at 20 °C on OCs/IL un-doped mixtures (no Li salt present). Fig. 3 shows the behaviour of both viscosity and conductivity against the IL content in the un-doped mixtures. Concerning the viscosity, a remarkable decrease of η is observed when an amount of 20 vol% of EC/DEC is added to the IL. In the IL composition range between 80 and 40 vol% the viscosity remains substantially constant around 25 mPa s, but it further decreases below 40 vol%. The conductivity follows the expected inverse trend, however a monotonous increase is observed

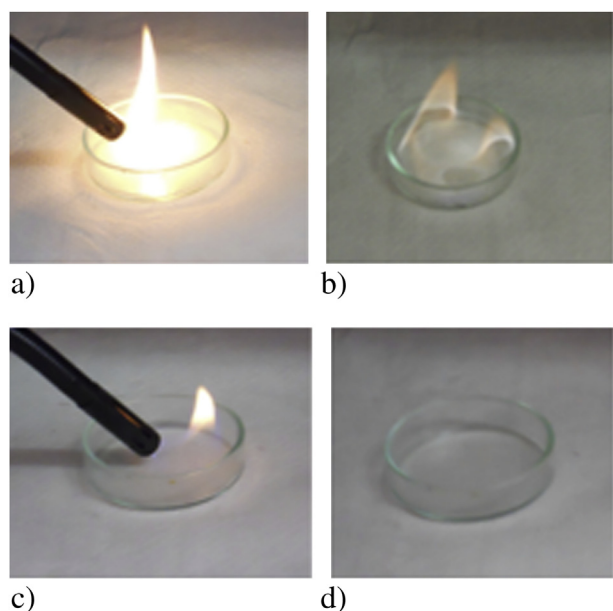


Fig. 1. Flammability tests on the 1.0 M LiPF₆ EC/DEC commercial electrolyte (a, b) and on MIX60 (c, d).

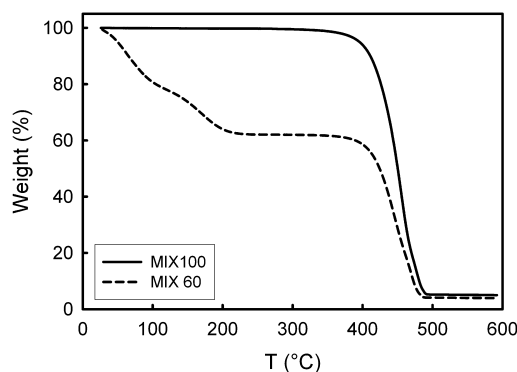


Fig. 2. TGA plots of two electrolytes, the pure Li–IL system (MIX100) (solid line) and MIX60 (dotted line).

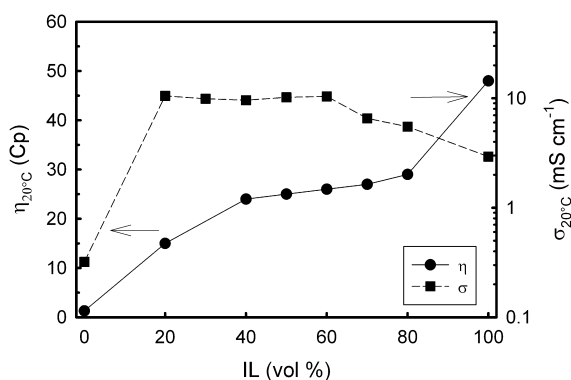


Fig. 3. Conductivity (squares) and viscosity (circles) vs. the ionic liquid content in the un-doped mixtures (no Li salt present), measured at 20 °C. The lines are only a guide for the eye.

passing from 100 vol% to 60 vol% of IL. At higher OCs concentration, it remains constant, in fair agreement with the viscosity data, reaching values of about 10 mS cm⁻¹ at 20 °C. As expected, the conductivity of the pure EC/DEC binary system is lower than that of the pure IL, due to the presence of very few ions, coming from auto-ionization phenomena [17].

By comparing the physical properties of the Li⁺-free mixtures, as illustrated in Fig. 3, only three compositions seem to be suitable in terms of high conductivity, low viscosity and reduced flammability. For these reasons, they were selected as solvent mixtures for the preparation of three LiTFSI-based electrolytes (0.5 M), namely MIX70, MIX60 and MIX50 (see Table 1). Fig. 4 compares the conductivity Arrhenius plots of the three mixtures with those ones of LiTFSI–PYR_{1,201} (MIX100) and of the commercial electrolyte, 1.0 M LiPF₆ EC/DEC, in the temperature range between –20 °C and 80 °C. As expected from the viscosity values, which are substantially comparable to those ones of the non-doped systems (25–28 cPa), the addition of the organic solvents causes an increase of conductivity of about one magnitude order with respect to the IL–LiTFSI system. No important differences are, in contrast, found by changing the composition of the mixture, and values around 7–8 mS cm⁻¹ are easily reached at 20 °C (see Table 1).

The behaviour of the conductivity is well described by the Vogel–Tammann–Fulcher (VTF) equation [25],

$$\sigma(T) = AT^{-0.5}e^{-\frac{B}{T-T_0}} \quad (1)$$

where A is the pre-exponential factor, T_0 is a reference temperature which usually falls in the range 20–50 K below the T_g , and B is a pseudo-activation energy for the charge-carriers motion. The VTF

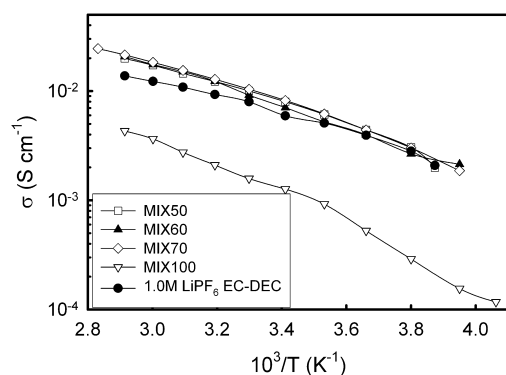


Fig. 4. Conductivity Arrhenius plots of the investigated electrolytes between –20 °C and 80 °C. The lines are only a guide for the eye.

equation (1) is a phenomenological way to interpret ion transport (or viscosity) data in amorphous polymer electrolytes above the glass transition [26]. In particular, VTF behaviours of viscosity and conductivity are frequently reported for ionic liquids [27,28]. Empirically, the VTF parameters can be obtained by fitting the conductivity data in terms of a linearized relationship. The values of the best-fitting parameters, A , B and T_0 , for the liquid electrolytes are reported in Table 1. All the parameters are affected by the presence of the organic carbonates. The pseudo-activation energies are generally near to the value calculated for the PYR_{1,201}-based liquid electrolyte ($B = 568$ K) [15]. T_0 values in the range 118–170 K have been determined for the electrolytes, in good agreement with the calorimetric glass transition temperatures obtained by DSC (see Table 1). They substantially decrease by increasing the amount of organic solvents in the mixture.

3.3. The electrochemical stability

The electrochemical stability of the studied electrolytes has been explored at room temperature in terms of both cathodic and anodic limits for the mixtures as well as the pure systems doped with a LiTFSI concentration of 0.5 M. Fig. 5 shows as an example the electrochemical windows of the samples MIX50 and MIX60. The data were collected between the OCV and 6.0 V vs. Li/Li⁺ for the anodic side and 0 V vs. Li/Li⁺ for the cathodic one. The mixtures show limit potentials which are slightly affected by the OCs amount in the solution. The most stable system is MIX60, which does not exhibit any oxidation phenomenon up to 4.5 V. In this case, an overall electrochemical window higher than 4 V is obtained, similarly to what observed for the PYR_{1,201}TFSI–LiTFSI system [13–15].

Fig. 6a compares the behaviour of the interfacial resistance, R_i , with the storage time for MIX50, MIX60 and MIX70, obtained by means of impedance spectra in a symmetrical Li/MIX/Li cell. As typically observed in these systems, the interfacial resistance, which includes the charge transfer resistance and the resistance of the passivation layer (SEI) on the electrode surface, immediately increases after the cell assembly [29,30]. This phenomenon is related to the fast formation, evolution and completion of passivation layers on the lithium electrodes. However, contrary to the IL–LiTFSI system, where a very unstable and highly resistive SEI is formed ($R_i > 8000 \Omega$), the interfaces of both MIX50 and MIX60 remain quite stable around 700 Ω and 500 Ω , respectively. In Fig. 6b the impedance Nyquist plots, collected at room temperature, are reported for the system with MIX60 electrolyte. Generally speaking, even the bulk resistance, given by the high frequency intercept with the real axis, remains stable during the storage time. Only after 20 days a slight decrease in conductivity is detected,

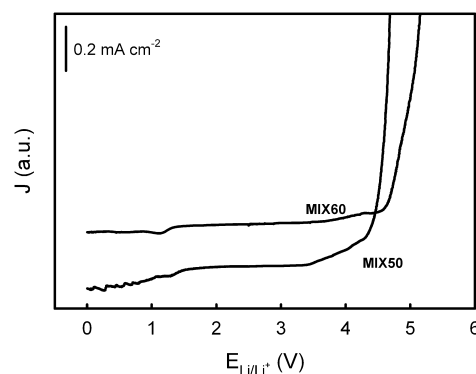


Fig. 5. R.t. sweeps of linear voltammetry of two electrolytes, MIX60 and MIX50, respectively. Li was used as the counter and reference electrode and Ni as the working one. Scan rate: 0.2 mV s⁻¹.

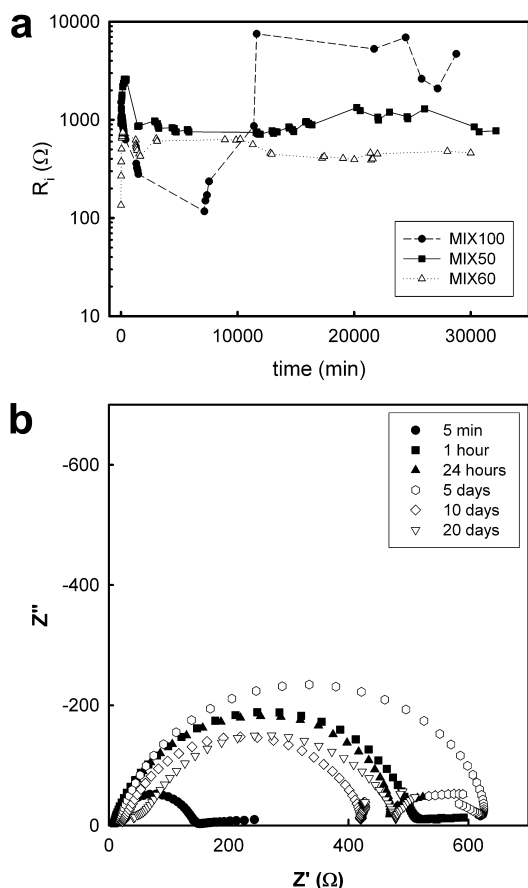


Fig. 6. (a) Time evolution of the interfacial resistance (R_i) at room temperature for MIX100 (circles), MIX60 (squares) and MIX50 (triangles) in a Li/electrolyte/Li symmetrical cell. The lines are only a guide for the eye. (b) Nyquist plots obtained by means of impedance spectroscopy on the Li/MIX60/Li cell at r.t. and at different storage times.

which may be reasonably due to some compositional changes of the species involved in the ion transport, occurring when the passivation film is formed.

In the lights of these results, namely a high ionic conductivity combined to a wide electrochemical window and high interfacial stability, we can conclude that the MIX60 electrolyte seems to be the best candidate as an electrolyte in lithium batteries. For this reason, it was selected for the battery tests, discussed in the following section.

3.4. Battery tests

Fig. 7a shows the performances at room temperature of a Li cell employing MIX60 as the electrolyte and LiFePO_4 as the cathode. Both charging and discharging rates were varied between 0.05 C and 2 C. The behaviours of a reference electrolyte, namely 1.0 M LiPF_6 EC–DEC, as well as that of the pure IL-based system are reported for the sake of comparison. As shown in the figure, at low current rates similar performances were obtained for the cells including MIX60 and the commercial solution, with capacity values, namely 155 mA h g^{-1} and 160 mA h g^{-1} respectively, fairly close to the theoretical one. In contrast, in case of $\text{PYR}_{1,201}\text{TFSI-LiTFSI}$ 0.5 M (MIX100), the cell provided capacities around 90 mA h g^{-1} , which are remarkably lower than those observed for the other systems, in spite of a comparable electrochemical stability. Such a difference may be interpreted in terms of poorer electrode wettability, likely due to the presence of the more viscous

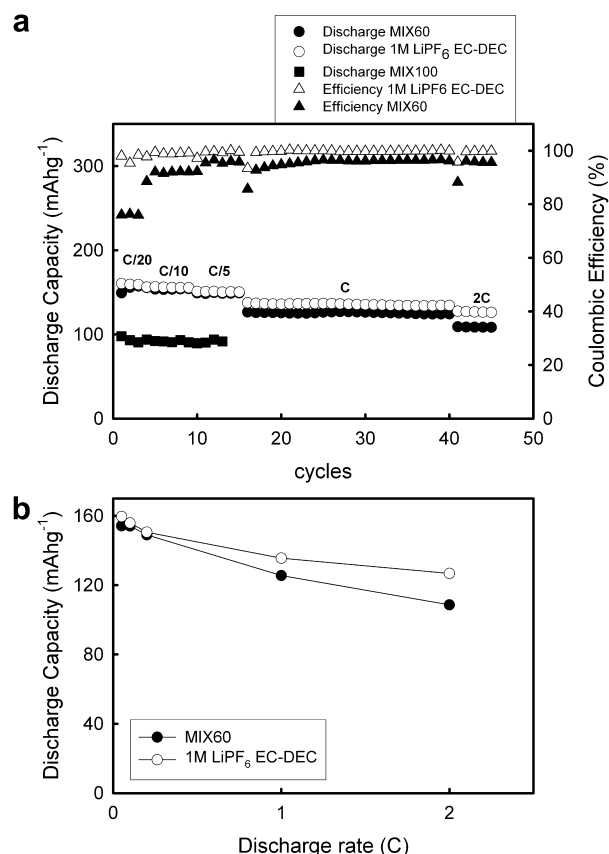


Fig. 7. (a) Room temperature cycling behaviour (discharge capacity and efficiency) of Li/LiFePO₄ cells containing the commercial electrolyte 1.0 M LiPF_6 EC/DEC (open circles) and MIX60 one (filled circles). (b) Discharge capacity vs. the discharge rate for the same cells described in (a).

ionic liquid [19]. For what concerns the cycling efficiency, values very close to the unity were detected at each C rate in case of the commercial electrolyte-based cell. In case of the MIX60, in contrast, the charging/discharging efficiency reached, at best, 97% and the transients at C rate changes were much more pronounced. Again, this difference may be related to the reduced electrode wettability.

Fig. 7b shows the behaviour of the specific capacity vs. the C rate for both the MIX60 electrolyte and the commercial one. No remarkable differences are noted between the two systems, at least up to medium C regimes. When the cells are cycled at 2 C, capacity retentions of 70% in case of MIX60 and 75% for the reference electrolyte are still measured, corresponding to a specific capacity of 109 mA h g^{-1} and 128 mA h g^{-1} , respectively.

Finally, the long-term stability of the MIX60 electrolyte was checked at 1 C for more than 250 cycles on a freshly prepared cell. Before the constant cycling, the cell was subjected to some initial cycles at 0.1 C. Fig. 8 shows the charge/discharge capacity and the coulombic efficiency of this cell. It is interesting to note that the specific capacity delivered at 1 C is $\sim 10\%$ higher than that obtained at the same C rate during the cycling tests showed in Fig. 7a and b. In fact, values of about 145 mA h g^{-1} were delivered at least for 130 cycles, although with some fluctuations, and reduction down to 135 mA h g^{-1} were observed after 250 cycles, with an overall capacity retention higher than 90% and cycling efficiency very close to the unity. This phenomenon is frequently observed in literature, in presence of ionic liquids as electrolytes, and it is generally interpreted in terms of non-optimal electrode wettability, which may be improved by pre-cycling steps [19].

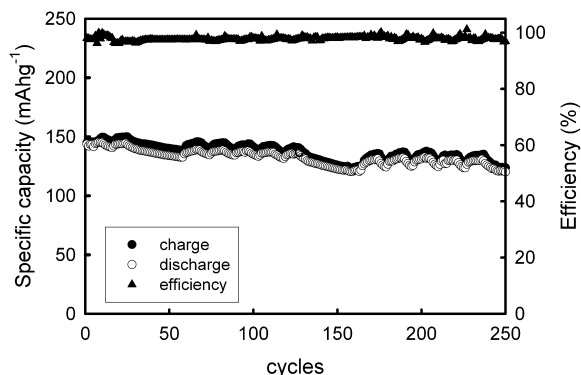


Fig. 8. Specific capacity and cycling efficiency of a LiFePO_4 -based cathode combined with the MIX60 electrolyte. The cell was cycled at r.t. with a charge/discharge rate corresponding to 1 C.

We can, therefore, infer that the electrolyte is not the limiting factor in determining the specific capacity, at least up to 1 C, and that the reduction observed in Fig. 7 when changing the C rate is likely due to uneven SEI formation and/or poor electrode wettability.

4. Conclusions

$\text{PYR}_{1.201}\text{TFSI}$ and EC/DEC binary mixtures were prepared with three different volume ratios, namely 70:30, 60:40 and 50:50 (IL:OCs) and doped with LiTFSI (0.5 M) in order to investigate their performances as potential safer electrolytes for lithium batteries. The combination of the beneficial effects of both the solvents brought to solutions with remarkably reduced flammability and promising physical and electrochemical properties. In particular, MIX60 resulted to be the best compromise, with ionic conductivity exceeding 7 mS cm^{-1} at 20°C , room temperature viscosity lower of about 25 cPs and an overall electrochemical window of 4.5 V. With respect to the pure LiTFSI–IL electrolyte, a very stable interface with Li anode is also observed in case of MIX60 electrolyte at least for 20 storage days.

LiFePO_4 -based cell including MIX60 as the electrolyte displayed good performances when cycled at room temperature between 0.1 C and 2 C. Discharge capacity higher than 100 mA h g^{-1} was delivered even at the higher rate regime. Values ranging between 135 and 145 mA h g^{-1} were displayed at 1 C for more than 245 cycles, with an overall capacity retention of 93% and a charge/discharge efficiency very close to the unity.

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